Degradation of sunscreen agent 2-phenylbenzimidazole-5-sulfonic acid by TiO$_2$ photocatalysis: Kinetics, photoproducts and comparison to structurally related compounds

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ABSTRACT

The wide occurrence of sunscreen agent micropollutants in natural environment received extensive attention in recent years due to their potential endocrine disrupting effect. The present study focuses on the kinetics and mechanism of photocatalytic degradation of sunscreen agent 2-phenylbenzimidazole-5-sulfonic acid (PBSA) in illuminated TiO$_2$ suspensions. Photocatalysis of PBSA was systematically investigated under different process conditions and water matrices. Experimental results demonstrated that PBSA photocatalytic reactions followed pseudo-first-order kinetics. Radical scavenging experiments indicated that hydroxyl radical (HO$^\bullet$) is the predominant reactive species responsible for an appreciable degradation of PBSA. Second-order rate constant of PBSA-HO$^\bullet$ reaction was determined to be 5.8×10^9 M^{-1} s^{-1} by competition kinetics method. Major intermediates included hydroxylated products, benzamide, hydroxylated benzamidine, hydroxylated 2-pheny-1H-benzimidazole as well as phenylimidazolecarboxylic derivatives which were elucidated by means of high performance liquid chromatograph–mass spectrometry (HPLC–MS) technique. Four carboxylic acids, oxalic, malonic, acetic and maleic acids, were detected during PBSA photocatalysis by HPLC–UV analysis. Ion chromatography (IC) results revealed that the sulfonic group of PBSA was primarily converted to sulfate ion while nitrogen atoms were released predominantly as ammonium and to a lesser extent as nitrate. The reduction of TOC processed much more slowly compared to PBSA degradation, however, approximately 80% TOC was removed after 720 min irradiation. A comparison of photocatalytic degradation of PBSA and structurally related compounds revealed that the 5-sulfonic moiety in PBSA had negligible effect on the photocatalysis of 2-pheny-1H-benzimidazole while 2-phenyl substituent stabilized the benzimidazole ring system to photocatalytic degradation.

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1. Introduction

Sunscreens are widely used in personal care products (PCPs) in recent years due to the public awareness of protection against ultraviolet (UV) irradiation and skin cancer [1]. Sunscreens enter the aquatic environment directly as consequence of recreational water activities (e.g., bathing and swimming) or indirectly via wastewater treatment plants (WWTPs) as result of the use of cosmetics, showering, washing, rubbing off and excretion after dermal application [2,3]. The extensive use of sunscreens already led to frequent detection in many aquatic ecosystems with a considerably high concentration [2–4]. Indeed, sunscreens are regarded as a new kind of environmental contaminants according to the US Environmental Protection Agency [5]. Recent studies have provided evidence that organic sunscreens possess estrogenic properties and behavior as endocrine disrupting chemicals (EDCs) in the environment [6–12]. Furthermore, photo-induced transformation products of some kinds of sunscreens under natural solar irradiation were found to be more toxic than their parent species, which could be a further danger to the biota in environment [9]. Therefore, the long-term and extensive use of sunscreens may cause irreversible adversity on the ecology system.

2-Phenylbenzimidazole-5-sulfonic acid (PBSA), as one kind of sunscreen, is widely used in sunscreen formulations and cosmetics

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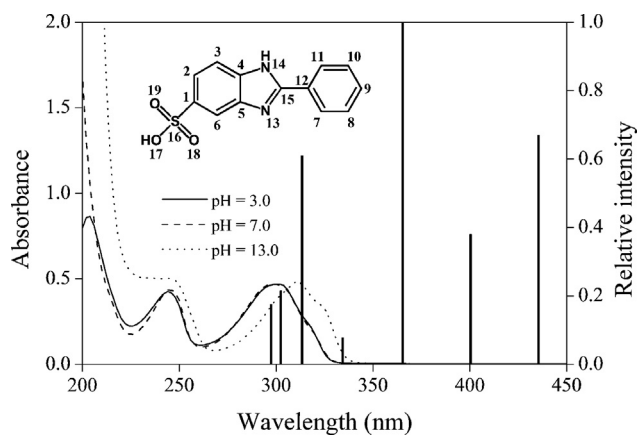
Fig. 1. UV–vis absorption spectra of 2-phenylbenzimidazole-5-sulfonic acid (PBSA) at different pH values and emission spectrum of HPK lamp. [PBSA] = 45 µM. Note that wavelength with $\lambda < 340$ nm was filtered by a 340 nm cut-off filter (0–52 Corning) to avoid direct photolysis of PBSA. The insert figure shows the chemical structure of PBSA, $C_{13}H_{10}O_3N_2S$. The atoms in PBSA molecular were labeled with numbers for the purpose of frontier electron density (FED) calculation.

because of its strong absorption in the UVB region (see Fig. 1). It has also been approved by the U.S. Food and Drug Administration as an effective sunscreen ingredient based on its ability to prevent erythema [1]. Due to its high polarity and continued input into the environment through personal care applications and incomplete elimination during wastewater treatment, PBSA was frequently detected in natural surface waters with a concentration ranging from 109 to 2679 ng L^{-1} [10]. PBSA has been known to photochemically generate reactive oxygen species (i.e., $^1O_2$ and $O_2^{\bullet-}$) under UV irradiation and cause DNA damage. For example, Johnson Inbaraj et al. reported that PBSA showed strong oxidizing properties when UV irradiated in neutral aqueous solution in the presence of cysteine, glutathione and azide [13]. Zhang et al. developed a computational method based on the density functional theory (DFT) to predict and evaluate the photodegradation behavior of PBSA and found that energy and electron transfer reactions of excited state PBSA (PBSA*) could photogenerate $^1O_2$ and $O_2^{\bullet-}$ [14,15]. Therefore, it is essential to develop advanced treatment technologies for eliminating PBSA in aqueous solutions for the sake of reducing potential risk to ecological system.

During the past years, various advanced oxidation processes (AOPs) have been reported for the decomposition of organic pollutants in aqueous matrices. Among them, heterogeneous semiconductor photocatalysis using TiO$_2$ as the photocatalyst has been found to be a promising treatment technology for eliminating organic pollutants, including sunscreens and other PCPs. When irradiating with photons of energy equal to or exceeding the band gap energy of TiO$_2$ (for anatase, 3.2 eV band gap), valence band holes (h_{vb}^+) and reductive conduction band electrons (e_{cb}^-) are generated [16,17]. The photogenerated holes can: (i) directly oxidize the adsorbed chemical substance; or (ii) produce adsorbed hydroxyl radical (HO$^\bullet$) via the surface-bound OH$^-$ and/or the adsorbed water molecules. As a highly reactive oxidant, HO$^\bullet$ is capable of unselectively reacting with most recalcitrant organic contaminants at near-diffusion-controlled rates in water (10^8–10^{10} M^{-1} s^{-1}). Therefore, TiO$_2$ is considered to be the most suitable semiconductor for widespread environmental photocatalytic applications because it is photoactive, non-toxic, inexpensive, and relatively biologically and chemically stable [16,17].

This study reports on the photocatalytic degradation of PBSA in aqueous suspensions of TiO$_2$. The main purpose of this study is to (i) study the influence of process condition and water matrix on photocatalytic degradation; (ii) clarify the dominant reactive species

involved in photocatalysis process; (iii) characterize intermediates and photoproducts; (iv) elucidate the mechanism and transformation pathways leading to PBSA mineralization; (v) compare with structurally related compounds in photocatalytic degradation. To the authors' knowledge, this is the first study that includes a systematic exploration of kinetics, intermediates and degradation pathways of PBSA photocatalytic degradation.

2. Experimental

2.1. Chemicals and materials

PBSA, 2-phenyl-1H-benzimidazole and benzimidazole were purchased from Sigma–Aldrich and used as received. Commercial humic acid (sodium salt) was purchased from Aldrich. HPLC grade methanol and acetonitrile were obtained from Fisher Scientific. Other reagents were at least of analytical grade and used as received without further purification. Non-porous titanium dioxide (Degussa P25 TiO$_2$, Germany) with primary particle diameter of 30 nm, specific surface area of 50 m^2 g^{-1} and crystal distribution of 80% anatase and 20% rutile was used as the photocatalyst for most of the experiments. Hombikat UV100 (100% anatase, 5 nm, 250 m^2 g^{-1}) and Aldrich rutile (100% rutile, 750 nm, 3 m^2 g^{-1}) were also used as photocatalysts in the preliminary experiment. Syringes (Injekt-F, 1 mL) were purchased form B. Braun. Millex-HV syringe filters (PVDF, 0.45 µm) were purchased from Millipore Corporation. All the solutions were prepared with 18 MΩ cm water from a Milli-Q water purification system.

2.2. Photocatalysis procedures

The photocatalytic experiments were performed in an open Pyrex glass cell with approximately 60 mL volume containing the aqueous suspension of TiO$_2$ powder and PBSA. The irradiation source was a high pressure mercury lamp (HPK 125W, Heraeus) with maximum emission wavelength mainly around 365 nm. Infrared radiation (IR) was well filtered by water circulation in the reactor jacket which maintained the temperature at 20 ± 1 °C. Direct photolysis caused by UV irradiation was avoided by using a 340 nm cut-off filter (0–52 Corning). The radiant flux entering the reactor was measured directly by a VLX-3W radiometer with a CX-365 detector (UV-A) and was found to be approximately 3.32 mW cm^{-2}. A volume of 25 mL aqueous solution containing PBSA and TiO$_2$ powder with required concentration was introduced in the reactor. Before irradiation, the suspension was magnetically stirred in the dark for 30 min to reach adsorption–desorption equilibrium. During irradiation, aliquots of samples (~300 µL) were withdrawn with the help of syringe at various intervals and filtered through syringe filters to remove TiO$_2$ particles before analysis. The adsorption of PBSA on filters was found to be negligible based on a preliminary test. Total volume of the samples withdrawn from each experiment was less than 10% (by volume) of the reaction solution. The pH of the reaction solution was adjusted by adding 0.1 M HClO$_4$ or 0.1 M NaOH.

2.3. Analytical procedures

A Shimadzu 10A series high performance liquid chromatography (Shimadzu, Japan) with a SPD-M10A DAD was employed to analyze the concentration of PBSA, 2-pheny-1H-benzimidazole, benzimidazole and benzoic acid, as well as the abundance of the photocatalytic degradation intermediates. The intermediates generated during photocatalysis of PBSA were analyzed by a HP 1100 series HPLC system equipped with a API 3000 triple quadrupole mass spectrometer (Applied Biosystems/MDS Analytical Technologies, Foster City, CA, USA) and coupled with a TurboIonSpray source
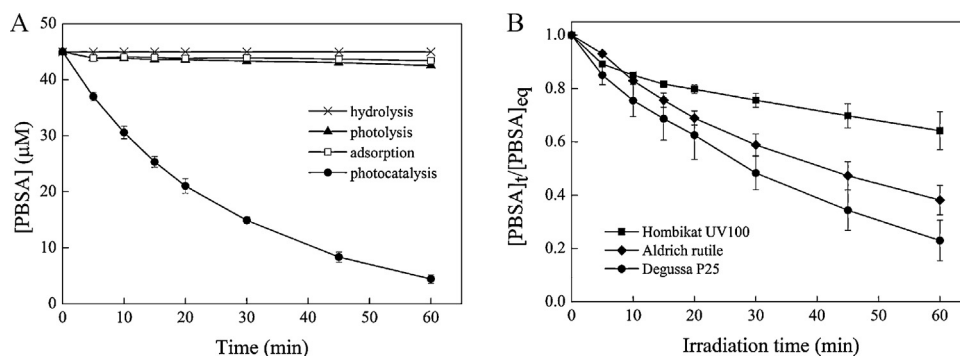
Fig. 2. (A) Comparison of hydrolysis, photolysis, adsorption and photocatalysis of PBSA in aqueous solutions. Degussa P25 TiO$_2$ was used as photocatalyst. [TiO$_2$] = 1.0 g L^{-1}; [PBSA] = 45 µM; pH = 7.0. (B) Effect of different photocatalysts on PBSA photocatalytic degradation. [TiO$_2$] = 1.0 g L^{-1}; [PBSA] = 45 µM; pH = 4.5. Error bars represent 95% confidence intervals.

(TIS) operated in positive ion mode for the MS measurements. The detection of carboxylic acids was performed using a HPLC–UV system (Varian 9010 model) equipped with a ICSep-GOREGEL-87H3 cation exchange column (9 µm, 300 mm × 7.8 mm, i.d.) (Transgenomic, USA). The analyses of inorganic ions released during photocatalysis process were carried out by using a Metrohm ion chromatographic instrument (881 Compact IC Pro, Switzerland). To determine the extent of mineralization during photocatalysis, total organic carbon (TOC) of filtered suspension samples was measured using a TOC-5050A analyzer (Shimadzu). The UV–vis absorption spectra of PBSA and humic acid aqueous solutions were recorded using a Lambda 950 UV-vis spectrophotometer (PerkinElmer, USA) equipped with quartz cuvettes (optical path length 1.0 cm). The pH of the solutions was measured with a combined glass electrode connected to a PHM 210 standard pH meter (Radiometer, Copenhagen, Denmark). The analytical details are presented in the Supplementary Data.

2.4. Determination of second-order rate constant of PBSA-HO• reaction

The second-order rate constant for reaction of PBSA with HO• was determined by competition kinetics method using Fenton's reagent as HO• generation source [18]. The detailed procedure is shown in the Supplementary Data.

2.5. Calculation of frontier electron density of PBSA

Molecular orbital calculations were carried out at the single determinant (B3LYP/6-311+G*) level with the optimal conformation having a minimum energy obtained at the same level in a Gaussian 09 program. The frontier electron densities (FEDs) of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were determined. Values of $FED_{HOMO}^2 + FED_{LUMO}^2$ were calculated to predict the reaction sites for hydroxyl addition.

3. Results and discussion

### 3.1. Preliminary experiments of PBSA photocatalytic degradation

Preliminary experiments of hydrolysis (without TiO$_2$ in dark), direct photolysis (without TiO$_2$ under irradiation) and adsorption (with TiO$_2$ in dark) were carried out to assess their contribution to photocatalytic degradation of PBSA by Degussa P25 TiO$_2$ as presented in Fig. 2A. As seen, no loss of PBSA was observed due to hydrolysis, suggesting PBSA was stable in Milli-Q water under dark condition. Dark controls also indicated that PBSA was stable in aqueous solution with pH ranging from 3 to 13 without light.

Direct photolysis of PBSA in Milli-Q water contributed to a negligible degradation of PBSA (less than 5%), which can be attributed to an unappreciable overlap of PBSA UV–vis absorption spectrum ($\lambda < 340$ nm) and the emitting spectrum (340–800 nm) of the filtered HPK lamp used as irradiation source in our study (see Fig. 1). Adsorption of PBSA on TiO$_2$ was also found to be marginal probably due to the relatively high hydrophilicity of PBSA (solubility 0.26 g L^{-1}). Therefore, hydrolysis, direct photolysis and adsorption contributed insignificantly to the decay of PBSA in comparison to photocatalysis.

In order to choose the most suitable catalyst for PBSA photocatalytic degradation, experiments using different kinds of catalysts (i.e., Degussa P25, Aldrich rutile and Hombikat UV100) were carried out (Fig. 2B). As seen, photocatalytic degradation of PBSA proceeded much more rapidly in the presence of P25 relative to other photocatalysts. The photoreactivities of these catalysts followed the order Degussa P25 > Aldrich rutile > Hombikat UV100. The substantially higher activity of P25 is not unexpected, since similar results were observed by other authors [19,20]. The low re-combination rate of photogenerated electrons and holes due to a mixture crystal structure of P25 compared to other pure crystal catalyst is believed to be responsible for a significantly higher photoactivity [20]. However, it should be noted that the photocatalytic activity of TiO$_2$ depends on various parameters in a complex way (e.g., crystallinity, surface, particle size, defect sites, surface charge) [21]. Recent studies also have shown that the photocatalytic activity of TiO$_2$ is highly substrate-specific [22]. Concerning the preliminary experiment result, our subsequent runs were carried out using P25 as photocatalyst.

3.2. Determination of major reactive species

Preliminary experiment demonstrated that TiO$_2$ mediated photocatalysis was responsible for an appreciable degradation of PBSA. During photocatalysis process, photo-excited separation of valence band holes (h_{vb}^+) and reductive conduction band electrons (e_{cb}^-) occur when TiO$_2$ absorbs photons with energy larger than band gap. The highly oxidative h_{vb}^+ can be transferred to the surface-adsorbed water or hydroxyl groups (i.e., titanol group) to form the surface-bound hydroxyl radical (HO•$_{surf}$) or free hydroxyl radical (HO•$_{free}$) after desorption from the surface. On the other hand, e_{cb}^- transfers to dissolved oxygen, leading to the production of superoxide radical anion (O$_2$•$^-$) and hydroperoxyl radical (HO$_2$•) and its further reduction to hydrogen peroxide (H$_2$O$_2$) [23–25]. Among them, HO• (either adsorbed or free) is often assumed to be the major species responsible for the photocatalytic oxidation, based on the evidences including detection of hydroxylated intermediates, distribution of the hydroxylation products, and spin trapping with subsequent ESR detection [24]. On the other hand,
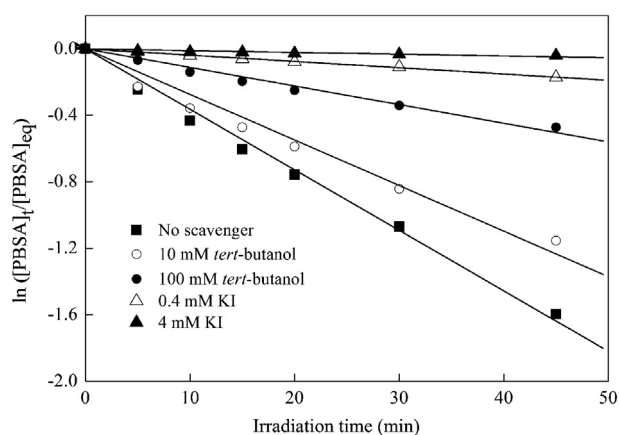
Fig. 3. Effect of radical scavengers on PBSA photocatalytic degradation. The *tert*-butanol was used as a scavenger of HO• while KI was used as a scavenger of both h_{vb}^+ and HO•. Experimental conditions: Degussa P25 TiO$_2$ was used as photocatalyst; $[TiO_2] = 2.0\,g\,L^{-1}$; $[PBSA] = 37.9\,\mu M$; pH = 4.5.

direct hole oxidation through electron transfer is also feasible since the oxidation potentials of most organic compounds lie below that of h_{vb}^+. For example, carboxylic acids, lacking abstractable hydrogens or C—C unsaturation, are believed to be oxidized primarily by h_{vb}^+ via a photo-Kolbe process [26].

In order to verify the photocatalysis mechanism and distinguish the contribution of these reactive species, radical scavengers are usually employed as diagnostic tools to investigate the importance of certain kind of radicals since these scavengers selectively react with radicals to form stable or persistent intermediates [26–29]. For example, alcohols such as isopropanol, methanol and *tert*-butanol, have been commonly used to estimate HO• mediated mechanism [26,27]. The direct oxidation of these alcohols by h_{vb}^+ is believed to be negligible because they have a very low affinity to TiO$_2$ surface in aqueous solution [27]. Iodide ion is an excellent scavenger that reacts with h_{vb}^+ and adsorbed HO• because h_{vb}^+ can be easily captured by I$^-$ (an electron donor) and oxidation of I$^-$ by surficial HO• is also possible [28,29].

In this study, *tert*-butanol, as a scavenger of HO• ($5.0 \times 10^8\,M^{-1}\,s^{-1}$) [23], and potassium iodide (KI), as a scavenger of both h_{vb}^+ and HO• ($1.2 \times 10^{10}\,M^{-1}\,s^{-1}$) [28] were used and the results are shown in Fig. 3. It was observed that PBSA photocatalysis reactions with or without radical scavengers all followed pseudo-first-order kinetics. The obtained pseudo-first-order rate constants as well as corresponding linear correlation coefficient are presented in Table S2 (Supplementary Data).

In Fig. 3, the control run (no scavenger) exhibited a degradation rate constant of 0.0486 min^{-1}, resulting from combined effects of all the possible radicals. However, the degradation rate constant decreased more than 92% and 97% in the presence of 0.4 mM and 4 mM KI, respectively. This suggests that both HO• and h_{vb}^+ together were responsible for the major degradation of PBSA, while other radicals such as O$_2$•−, HO$_2$• and H$_2$O$_2$ contributed insignificantly to PBSA degradation. To determine the relative contribution between HO• and h_{vb}^+, further runs using *tert*-butanol as HO• scavenger were carried out. In Fig. 3, the addition of 10 mM and 100 mM *tert*-butanol resulted in a degradation rate constant of 0.0274 min^{-1} and 0.0112 min^{-1}, respectively, which decreased by 43% and 77% compared with control run. Hence, HO• was likely to be the most important radical during PBSA photocatalytic degradation. It is believed that reaction with holes is more important for hydrophobic compounds that are repelled from the aqueous solution and are thus more likely to undergo adsorption on the photocatalyst surface [22]. Therefore, the relatively higher hydrophilicity of PBSA and lower adsorption may be one reason accounting for the less

importance of h_{vb}^+. Since HO• is highly electrophilic, we speculate that the rich π electron system of benzimidazole and phenyl moiety of PBSA molecular favor HO• attack, which in turn enables HO• playing a more important role than other radicals. This hypothesis is further verified by the intermediates that were identified by LC–MS.

Second-order rate constant of PBSA-HO• reaction was determined by competition kinetic method as described in Section 2 according to the following equation [29].

$$\ln\left(\frac{[PBSA]_t}{[PBSA]_0}\right) = \frac{k_{HO•,PBSA}}{k_{HO•,BA}}\ln\left(\frac{[BA]_t}{[BA]_0}\right) \tag{1}$$

where BA is the reference compound, benzoic acid, with a known rate constant of reaction with HO• ($k_{HO•,BA} = 5.9 \times 10^9\,M^{-1}\,s^{-1}$) [29]. From Eq. (1), the second-order rate constant of PBSA-HO• reaction was calculated to be $5.8 \times 10^9\,M^{-1}\,s^{-1}$ by plotting of ln([PBSA]$_t$/[PBSA]$_0$) versus ln([BA]$_t$/[BA]$_0$) (see Fig. S1, Supplementary Data). Such a high second order rate constant suggests that PBSA could readily react with HO• near the diffusion-controlled limit. This observation further supports the result of radical scavenging experiment, that, HO• is the most important radical involved in PBSA photocatalysis.

3.3. Effect of process conditions and water matrices on PBSA photocatalytic degradation

Further batch experiments under different process conditions (i.e., catalyst loading, initial substrate concentration and solution pH) were performed for the purpose of a systematic study and the obtained overall results are summarized in Table 1. Our results reveal that photocatalytic degradation of PBSA under different operation conditions followed pseudo-first-order kinetics.

For the TiO$_2$ loading, the initial reaction rate r_0, which was calculated over the course of first 5 min of irradiation, increased with increasing catalyst loading up to a certain value, while further increasing the catalyst loading significantly reduced r_0 (Table 1). It is proposed that with TiO$_2$ dosage increasing, more photons are expected to be absorbed by TiO$_2$, which consequently leads to higher amount of reactive species [17]. The enhanced concentrations of reactive species are generally responsible for a much faster degradation. However, when TiO$_2$ loading was higher than 2.0 g L^{-1}, a decreased r_0 was observed which can be explained by screening effect of excess particles, masking part of the photosensitive surface, as well as scattering or reflecting the amount of photons needed for exciting the catalyst [30,31]. In addition, a higher TiO$_2$ loading usually leads to aggregation of the photocatalyst particles that decreases the contact surface area between reactant and photocatalyst, and consequently, reduces the number of active sites and lowers the rate of photodegradation [32].

Previous studies have reported the dependency of the TiO$_2$ photocatalytic reaction rate on the concentration of the organic substrate [20,30,31]. Table 1 also illustrates the effect of different initial concentration of PBSA on the initial reaction rate r_0. As seen, r_0 increased as the concentration of PBSA increased up to a maximum value, while further elevating the concentration led to a decreased reaction rate. The enhancement of r_0 with increasing PBSA concentration could be explained by the scavenging of reactive species by the substrate. The reaction of PBSA with HO• and h_{vb}^+ on the surface of TiO$_2$ is in competition with the thermal recombination process HO•/e$_{cb}^-$ and h_{vb}^+/e$_{cb}^-$. An excessive concentration of PBSA could completely inhibit the unfavorable recombination, thus, the initial reaction rate of PBSA can be expected to reach a maximum value equivalent to the trapping rate of HO• and h_{vb}^+ on TiO$_2$ surface. During photocatalysis process, organic compounds generally transform to radical transient at the first step by reacting with h_{vb}^+ and HO• (e.g., HO• adduct or

Table 1
Results of batch experiments for degradation of PBSA by TiO$_2$ photocatalysis.

Photocatalyst	TiO$_2$ (g L^{-1})	C_0 (μM)[a]	pH[b]	HCO$_3^-$ (mM)	HA[c] (mg L^{-1})	k_p (min^{-1})[d]	r_0 (μM min^{-1})[e]	R^2 [f]
1. Effect of photocatalyst type								
Aldrich rutile	1.0	45	4.5	0	0	0.0184	–	0.999
Hombikat UV100	1.0	45	4.5	0	0	0.0095	–	0.969
Degussa P25	1.0	45	4.5	0	0	0.0285	–	0.998
2. Effect of photocatalyst loading								
Degussa P25	0.25	37.9	4.5	0	0	–	1.14	–
Degussa P25	0.5	37.9	4.5	0	0	–	1.47	–
Degussa P25	1.0	37.9	4.5	0	0	–	1.61	–
Degussa P25	1.5	37.9	4.5	0	0	–	2.20	–
Degussa P25	2.0	37.9	4.5	0	0	–	2.36	–
Degussa P25	3.0	37.9	4.5	0	0	–	0.94	–
3. Effect of substrate concentration								
Degussa P25	2.0	8.85	4.5	0	0	–	1.57	–
Degussa P25	2.0	22.1	4.5	0	0	–	1.63	–
Degussa P25	2.0	37.9	4.5	0	0	–	2.36	–
Degussa P25	2.0	44.3	4.5	0	0	–	2.06	–
Degussa P25	2.0	61.7	4.5	0	0	–	1.54	–
4. Effect of solution pH								
Degussa P25	2.0	37.9	2.5	0	0	0.0203	–	0.998
Degussa P25	2.0	37.9	4.5	0	0	0.0486	–	0.991
Degussa P25	2.0	37.9	8.5	0	0	0.0521	–	0.999
Degussa P25	2.0	37.9	10.9	0	0	0.0466	–	0.999
Degussa P25	2.0	37.9	11.3	0	0	0.0163	–	0.997
5. Effect of bicarbonate ion								
Degussa P25	2.0	37.9	8.5	1	0	0.0383	–	0.999
Degussa P25	2.0	37.9	8.5	10	0	0.0310	–	0.999
Degussa P25	2.0	37.9	8.5	100	0	0.0062	–	0.999
6. Effect of humic acid								
Degussa P25	2.0	37.9	5.5	0	6	0.0417	–	0.990
Degussa P25	2.0	37.9	5.5	0	18	0.0220	–	0.999
Degussa P25	2.0	37.9	5.5	0	60	0.0028	–	0.931

[a] The initial concentration of PBSA.
[b] The pH of the solutions was adjusted by 0.1 M HClO$_4$ or 0.1 M NaOH.
[c] HA represents humic acid.
[d] k_p is the pseudo-first-order rate constant.
[e] r_0 is the initial reaction rate which was calculated from the slope value of PBSA degradation curve over the first 5 min of reaction. r_0 was calculated instead of k_p for investigating the effect of catalyst loading and initial organic substrate on photodegradation efficiency.
[f] R^2 is the linear correlation coefficient.

H-abstract). These partially oxidized radical transient could either undergo further oxidation to a non-radical stable intermediate or react with an electron to return back to the initial substrate. The so-called back or recombination reaction will become dominant when the substrate concentration is high enough, which negatively contributes to a decreased initial reaction rate [33]. Considering the elevated initial concentration of PBSA, a larger yield amount of intermediates can also be expected, which are capable of poisoning the TiO$_2$ active sites and/or competing for photons with the catalyst, leading to a decreased transformation rate of mother compound [33].

The effect of solution pH on photocatalytic degradation is a complex issue related to the ionization states of organic compounds and the surface charge of catalyst as well as the formation rate of HO$^\bullet$ and other active radicals in the reaction solution [17,30]. The solution pH also alters the TiO$_2$ energy levels according to the Nernstian behavior (-59 mV/pH) due to the pH-dependent surface charge [25]. Since the point of zero charge (pH$_{pzc}$) of Degussa P25 is widely reported to be 6.25 and PBSA has two pK_a (i.e., p$K_{a1} = 4.0$ and p$K_{a2} = 11.9$) due to the presence of sulfonic and imidazole moiety in PBSA molecular [13], the predominant existing speciation of TiO$_2$

and PBSA in different pH solutions is according to the following equations.

$$TiOH + H^+ \leftrightarrow TiOH_2^+, \quad pH \leq pH_{pzc} \qquad (2)$$

$$TiOH + OH^- \leftrightarrow TiO^-, \quad pH \geq pH_{pzc} \qquad (3)$$
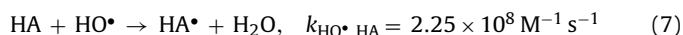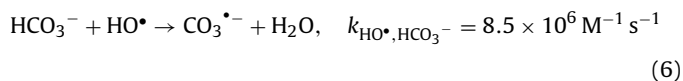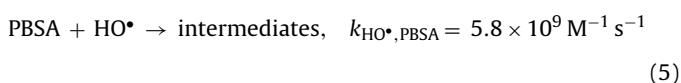

$$\qquad (4)$$

As shown in Table 1, photocatalytic degradation of PBSA is highly pH-dependent. At pH 2.5, the relatively low photodegradation rate constant was most likely due to the lack of electrostatic attraction between TiOH$_2^+$ and PBSA. Accordingly, the comparatively high rate constant at pH 4.5 can be attributed to the electrostatic attraction between TiOH$_2^+$ and PBSA-H, which facilitates the adsorption of PBSA on TiO$_2$ surface. However, the high rate constant at pH 8.5 was unexpected since electrostatic repulsion was expected to take place between TiO$^-$ and PBSA-H. Therefore, the pH-dependent effect of HO$^\bullet$ formation rate was likely responsible for such phenomenon because previous literatures have demonstrated that alkaline condition could promote photogeneration of hydroxyl radicals [19,34,35]. Nevertheless, at extremely high pH (pH = 13.0), the electrostatic repulsion between TiO$^-$ and PBSA-2H would become much stronger, which out-competed the positive effect of HO$^\bullet$ formation, and consequently decreased the degradation rate constant.
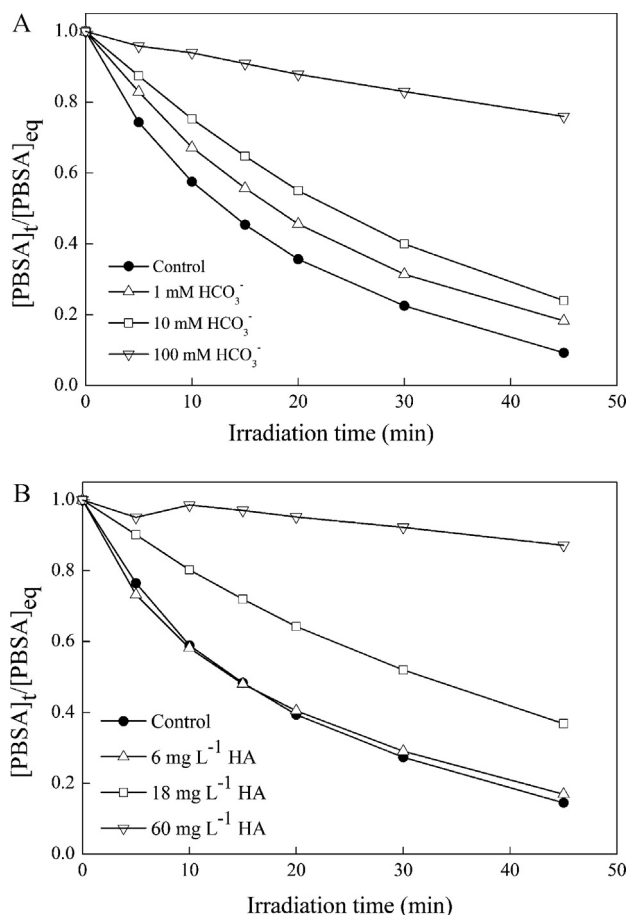
Fig. 4. Effect of (A) bicarbonate ion (pH = 8.5), and (B) humic acid (pH = 5.5) on PBSA photocatalytic degradation. Experimental conditions: Degussa P25 TiO$_2$ was used as photocatalyst; [TiO$_2$] = 2.0 g L^{-1}; [PBSA] = 37.9 μM; [HCO$_3^-$] = 0–100 mM; [HA] = 0–60 mM.

Water matrix plays an important role in photocatalytic degradation of organic compounds because some constituents that are ubiquitous in natural waters (e.g., bicarbonate ions, dissolved organic matter (DOM)) may serve as HO$^\bullet$ scavengers [36,37]. From this viewpoint, bicarbonate (HCO$_3^-$) and humic acid (HA) were chosen to investigate their effect on the photocatalysis degradation of PBSA since they are not only well-known HO$^\bullet$ scavengers but are also widely present in natural waters. Experiments were conducted in aqueous 37.9 μM PBSA solutions with a HCO$_3^-$ concentration range of 0–100 mM or a HA concentration rang of 0–60 mg L^{-1}. Note that, in the case of HCO$_3^-$, solution pH was maintained at 8.5 to ensure HCO$_3^-$ was the dominant species (pK_{a1} = 6.37 and pK_{a2} = 10.25) in the reaction solution.

It is evident that the presence of HCO$_3^-$ or HA suppressed the photocatalytic degradation of PBSA (Table 1 and Fig. 4). For example, PBSA transformation ratio was found to be only 24% and 12.2% after 45 min irradiation in the presence of 100 mM HCO$_3^-$ or 60 mg L^{-1} HA, respectively, compared to 92.4% and 85.5% in absence of HCO$_3^-$ (pH = 8.5) or HA (pH = 5.5), respectively. The inhibition can be ascribed to the competition for HO$^\bullet$ by HCO$_3^-$ and HA. It is assumed that if the PBSA coexists with HCO$_3^-$ or HA in reaction solution, the HO$^\bullet$ will be partitioned according to the following equations [38,39].

$$PBSA + HO^\bullet \rightarrow \text{intermediates}, \quad k_{HO^\bullet,PBSA} = 5.8 \times 10^9 \, M^{-1} \, s^{-1}$$

(5)

$$HCO_3^- + HO^\bullet \rightarrow CO_3^{\bullet-} + H_2O, \quad k_{HO^\bullet,HCO_3^-} = 8.5 \times 10^6 \, M^{-1} \, s^{-1}$$

(6)

$$HA + HO^\bullet \rightarrow HA^\bullet + H_2O, \quad k_{HO^\bullet,HA} = 2.25 \times 10^8 \, M^{-1} \, s^{-1}$$

(7)

Therefore, a fraction of HO$^\bullet$ will be quenched by HCO$_3^-$ or HA. If we assume that HO$^\bullet$ yield amount remained constant during photocatalysis, the increase in the concentration of HCO$_3^-$ or HA would lower the amount of HO$^\bullet$, leading less HO$^\bullet$ available for reacting with PBSA. For HA at higher concentration, competitive adsorption on TiO$_2$ active sites and light attenuating may also occur simultaneously (see Fig. S2, the adsorption mass (mg/g TiO$_2$) of HA on TiO$_2$ versus time and Fig. S3, the UV–vis absorption spectra of HA at different concentration, Supplementary Data) [40]. These factors may together retard PBSA photocatalytic degradation. Nevertheless, at lower concentration (e.g., 1 mM HCO$_3^-$ or 6 mg L^{-1} HA), the presence of HCO$_3^-$ or HA showed slight inhibition on PBSA photocatalysis. Since the environmentally relevant concentration of HCO$_3^-$ and HA are reported to be 0.4–4 mM and 0.3–30 mg L^{-1}, respectively [38,41], this observation is particularly interesting because of the feasibility of applying TiO$_2$ photocatalysis for treating PBSA micropollutant in environmentally realistic water matrix. It is worth noting that quenching of HO$^\bullet$ by HCO$_3^-$ yields carbonate radical (CO$_3^{\bullet-}$) (Eq. (6)), and CO$_3^{\bullet-}$ may react with PBSA due to its electron rich nature. However, no enhancement in photocatalytic degradation of PBSA was observed in this study as the HCO$_3^-$ concentration increased. Given that CO$_3^{\bullet-}$ is generally less reactive than HO$^\bullet$ (second-order rate constant for reaction of CO$_3^{\bullet-}$ with organic compound is normally 2–3 magnitude order lower than that of HO$^\bullet$) [38,39], it is possible that CO$_3^{\bullet-}$-mediated PBSA oxidation was negligible in the present study.

3.4. Identification of photodegradation intermediates and products

3.4.1. Evolution of organic intermediates

Advanced oxidation processes often yield various degradation intermediates and products due to the non-selective reaction of HO$^\bullet$ with organic pollutants. In this work, we have attempted to identify photodegradation intermediates using LC–MS technique. A mixture sample composed of aliquots withdrawn at different irradiation time was analyzed for the purpose of identifying as more intermediates as possible. Structural identification of these intermediates was based on the analysis of the total ion chromatogram (TIC) and the corresponding mass spectrum (Fig. S4 and Table S3, Supplementary Data). Major intermediates included hydroxylation products (mono-, di- and tri-hydroxylated PBSA), imidazole ring cleavage products (e.g., benzamide), and hydroxylated 2-pheny-1H-benzimidazole as well as phenylimidazolecarboxylic derivatives.

In order to correctly characterize mono-hydroxylated compounds (positions of hydroxylation), the frontier electron densities (FEDs) of PBSA (as PBSA-H form) were calculated to predict the reaction sites for HO$^\bullet$ attacking, and the obtained results are summarized in Table 2. In the Frontier Orbital Theory, the preferential HO$^\bullet$ addition probably takes place on the atom with the highest FED$_{HOMO}^2$ + FED$_{LUMO}^2$ value [42,43], which has been proved to be reasonable by the published work [44]. As shown in Table 2, 9C, 11C, 7C and 8C sites in phenyl ring and 2C in benzimidazole have the highest FED$_{HOMO}^2$ + FED$_{LUMO}^2$ value, implying both the two benzenes are likely to be attacked by HO$^\bullet$, resulting in the formation of mono-hydroxylation products. However, it should be noted that the possibility for HO$^\bullet$ addition to phenyl moiety is much higher than addition to benzyl moiety which is adjacent to imidazole.

Table 2
$FED^2_{HOMO} + FED^2_{LUMO}$ values of PBSA (PBSA-H form) atoms calculated by using Gaussian 09 program at the B3LYP/6-311+G* level.

Number (atom)[a]	$FED^2_{HOMO} + FED^2_{LUMO}$	Number (atom)	$FED^2_{HOMO} + FED^2_{LUMO}$
1C	0.0054	**11C**	**0.0927**
2C[b]	**0.0339**	12C	0.1916
3C	0.0151	13N	0.0722
4C	0.0130	14N	0.0451
5C	0.0021	15C	0.0438
6C	0.0280	16S	0.0001
7C	**0.0701**	17O	0.1793
8C	**0.0474**	18O	0.1996
9C	**0.2112**	19O	0.1877
10C	0.0306		

[a] See Fig. 1 for atom numbering.
[b] Atoms in bold means these atoms have the highest $FED^2_{HOMO} + FED^2_{LUMO}$ values, thus are more likely to be attacked by hydroxyl radical.

Although the 12C has a much higher $FED^2_{HOMO} + FED^2_{LUMO}$ value, we speculate that it is unlikely that the HO• will attack this site due to steric hindrance.

Fig. 5A describes the evolution profiles of five major intermediates of PBSA (i.e., mono-hydroxylated benzamidine (OH-BZMD); three isomers of mono-hydroxylated PBSA (OH-PBSA, A, C and E, respectively); and mono-hydroxylated 2-pheny-1H-benzimidazole (OH-PBI)) during photocatalytic degradation. As seen, all the intermediates quickly reached to maximum

concentration during 10–20 min followed by a gradually decay, indicating the formation and transformation of these intermediates were accompanied with the degradation of PBSA. Complete disappearance of these intermediates was observed after 90 min, suggesting TiO_2 photocatalysis is a promising technique for PBSA removal as well as intermediates elimination. The disappearance of the intermediates is also a reflection of further oxidation to low molecular weight organic compounds (e.g., carboxylic acids) or mineralization to inorganic ions.

3.4.2. Evolution of carboxylic acids

It is well-known that further oxidation of intermediates during photocatalysis usually leads to ring opening, generating a series of carboxylic acids with lower molecular weight before complete mineralization [16,31,35]. In this work, four major acids (i.e., oxalic, malonic, acetic and maleic acids) were identified by ion exchange chromatography by comparison with standards. Fig. 5B shows the evolution of these carboxylic acids as a function of irradiation time.

As seen, oxalic acid appeared as early as 30 min, and then gradually accumulated up to 57.8 μM at 210 min followed by a slow disappearance. The formation of oxalic acid can be explained either by the benzene ring opening or by dimerization of HCO_2 radicals as reported by previous studies [31]. Oxalic could be oxidized to two molecular of CO_2 by photo-holes through photo-Kolbe mechanism [16]. Since maleic acid has been known to be an important intermediate after ring opening [16], its detection in the present study was not unexpected. Malonic acid appeared at 60 min, reached a
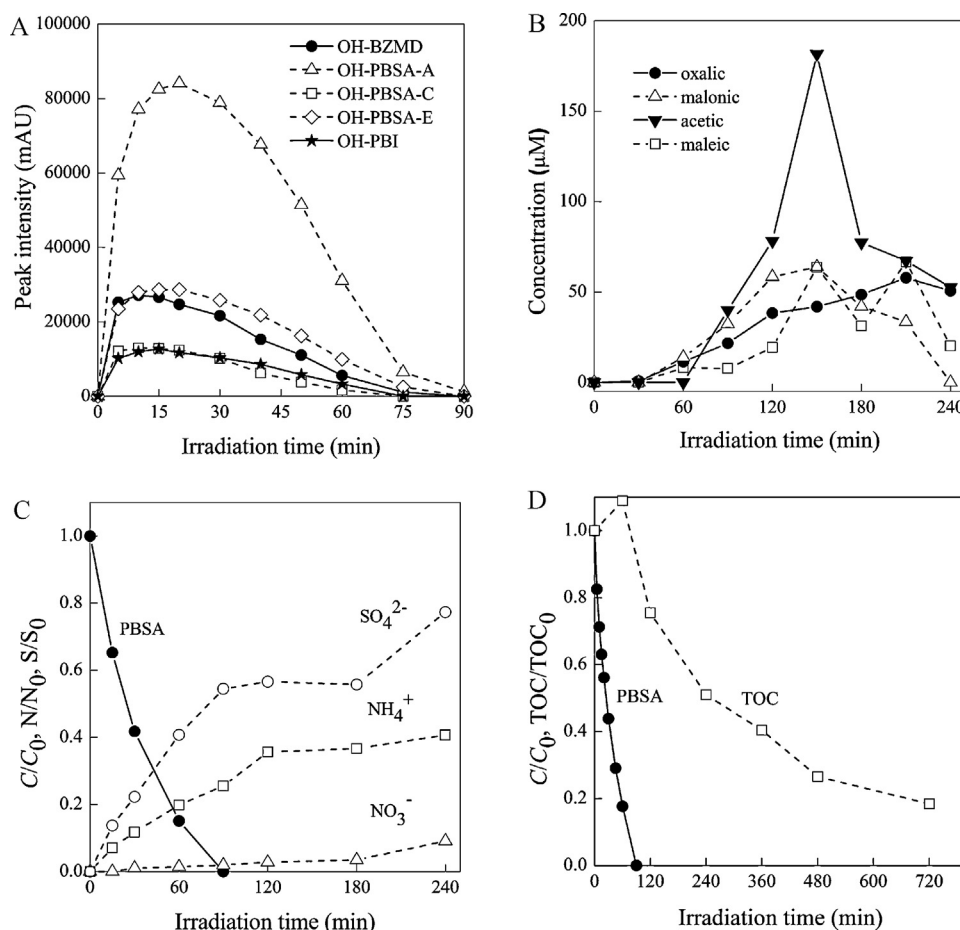
Fig. 5. Evolution of (A) organic intermediates, (B) carboxylic acids, (C) inorganic ions and (D) the variation of TOC during photocatalytic degradation of PBSA. Peak intensity was recorded according to HPLC–DAD spectrum. The detection wavelength was λ = 300 nm. OH-BZMD = mono-hydroxylated benzamidine; OH-PBSA = mono-hydroxylated PBSA; OH-PBI = mono-hydroxylated 2-pheny-1H-benzimidazole. Experimental conditions: Degussa P25 TiO_2 was used as photocatalyst; [TiO_2] = 2.0 g L^{-1}; [PBSA] = 45 μM; pH = 4.5.
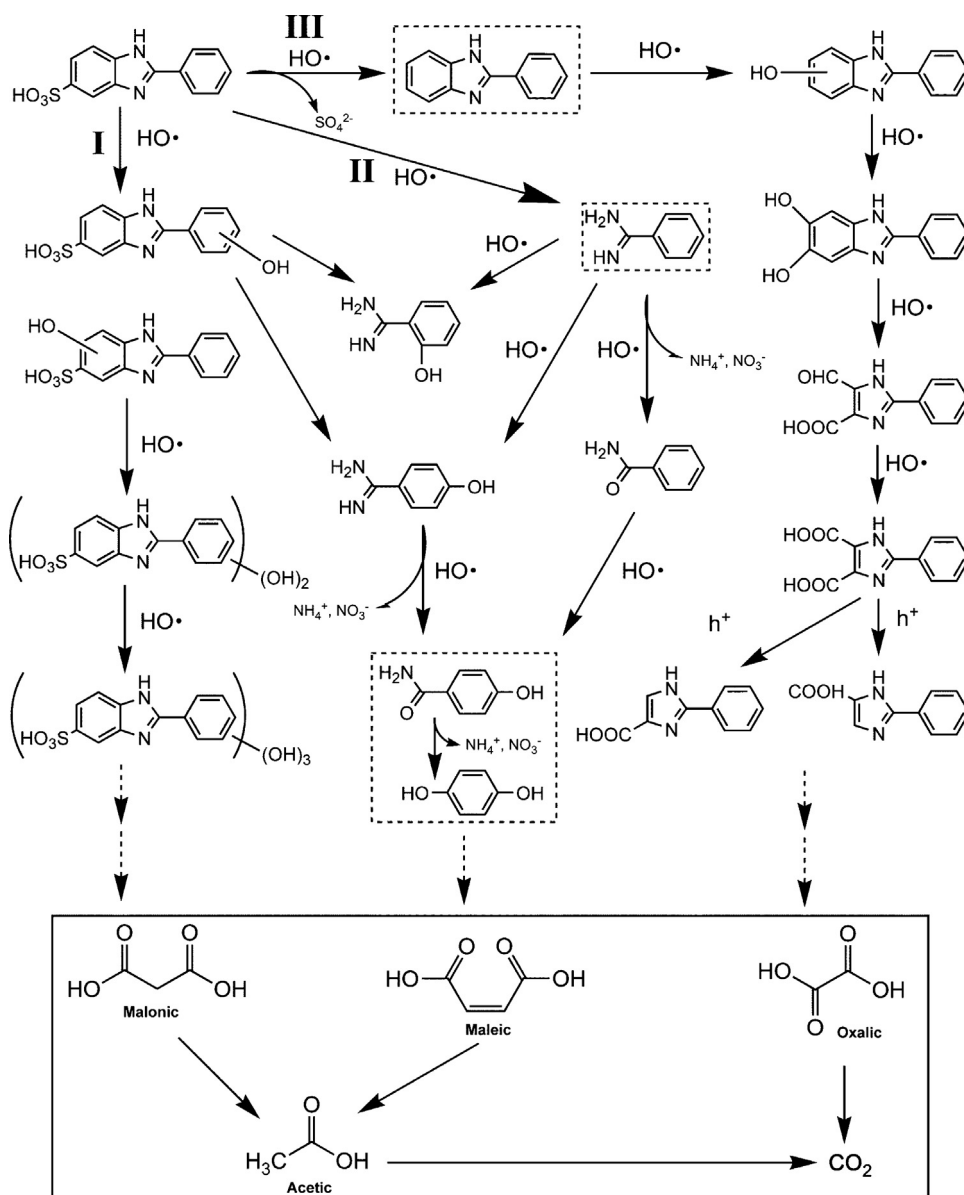
Fig. 6. Possible photocatalytic degradation pathways of PBSA in illuminated aqueous TiO_2 suspensions. Chemicals in dash line box were not detected in this work by using LC–MS but were previously reported [14,52]. Possible formation and transformation pathways of carboxylic acids were also elucidated as proposed in solid line box.

maximum (63.8 μM) at 150 min, and then gradually disappeared. Acetic acid was not observed until 90 min later and reached to maximum (181.6 μM) at 150 min, followed by a notable decrease. Note that the concentration of acetic was the highest among the four carboxylic acids. Therefore, acetic acid presumably resulted from the transformation of other carboxylic acids such as malonic and maleic acids [16]. Based on the above analysis, a description of the formation and transformation of carboxylic acids is presented in solid line box in Fig. 6.

3.4.3. Evolution of inorganic ions

Complete mineralization is the ultimate step in photocatalytic degradation of organic compounds. Thus, it is essential to investigate not only the disappearance of the initial pollutant but also its mineralization to CO_2 and inorganic ions. The evolution of inorganic ions during PBSA photocatalysis process is depicted in Fig. 5C. As clearly seen, sulfonic moiety in PBSA was converted to sulfate ions (SO_4^{2-}) while nitrogen atoms in imidazole structure were released as ammonium (NH_4^+) and nitrate (NO_3^-). At 90 min, 45 μM PBSA

was completely degraded, while only 25.5% and 1.9% of the nitrogen and 54.5% of sulfur were released as NH_4^+, NO_3^- and SO_4^{2-}, respectively. It is interesting to note that a majority of N was converted to NH_4^+ while only a minor amount of N was transformed to NO_3^-. This observation is consistent with previous reports that nitrogen in heterocyclic aromatic rings can be transformed to both NH_4^+ and NO_3^- species, while secondary, tertiary and quaternary nitrogen atoms are photo-converted predominantly to ammonium ions [45,46]. Increasing the irradiation time favors the releasing of inorganic species. At 240 min, 40.7% and 9.1% of the N and 77.3% of S were released as NH_4^+, NO_3^- and SO_4^{2-}, respectively. It is evident that less than 50% of total N was mineralized, indicating a significant amount of nitrogenated transformation products at the end of the treatment. Therefore, 240 min irradiation seemed to be not enough to yield a full mineralization. Unlike nitrogen, sulfur is expected to be quickly converted to SO_4^{2-} under the attack of $HO^\bullet$ as the following equation describes [47].

$$RSO_3^- + HO^\bullet \rightarrow HSO_4^- + R^\bullet \leftrightarrow H^+ + SO_4^{2-} + R^\bullet \tag{8}$$
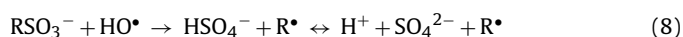
The reason for 77.3% S transformation ratio can be rationalized by the following: (i) complete mineralization of S containing organic intermediates was not obtained after 240 min irradiation, (ii) S atom was initially released as HS^- or SO_3^{2-} rather than directly oxidation to SO_4^{2-} [45], (iii) SO_4^{2-} was probably strongly adsorbed on TiO_2 active sites which led the detection amount below the stoichiometric value [48].

3.4.4. Mineralization

The photocatalytic degradation of organic pollutants usually leads to the decomposition of structure and eventually the mineralization to CO_2 and H_2O, which can be visualized by the decrease of TOC [49]. Fig. 5D shows the variation of TOC during photocatalytic degradation of PBSA. It was observed that TOC reduction processed much more slowly compared to the degradation of PBSA. This finding indicates the formation of more stable intermediates toward photo-oxidation [34]. However, approximately 80% TOC was removed after 720 min irradiation. Therefore, we can expect to have a mineralization at a very long irradiation time.

3.5. Elucidation of photocatalytic degradation pathways

Based on the elucidated molecular structure of photoproducts, possible TiO_2-induced photodegradation pathways of PBSA are proposed as illustrated in Fig. 6. As it can be seen, three major pathways, namely, successive hydroxylation of mother compound (Pathway I), imidazole ring cleavage (Pathway II) and de-sulfonic as well as further hydroxylation and oxidation (Pathway III), are involved in the photocatalytic degradation of PBSA.

(I) The successive addition of HO• to mother compound leads to the formation of mono-, di-, and tri-hydroxylated PBSA. A total five mono-hydroxylation, three di-hydroxylation and one tri-hydroxylation products were detected according to LC–MS spectrum. Since HO• is known to be electrophilic, the rich electron density of benzimidazole and phenyl ring may facilitate its addition. The calculated frontier electron densities revealed that both the two benzene moiety in PBSA molecular appeared to be susceptible to the electrophilic attack of the HO•, resulting in the formation of mono-hydroxylation. It is well accepted that hydroxylation is usually the first step, but also the most important step during photocatalysis. Hydroxylated organic compounds further undergo structure decomposition, such as ring opening and chain cleavage, which eventually lead to complete mineralization [50].

(II) The two N atoms in imidazole group have been reported to be the sites most likely attacked by HO• due to their much higher electron density [51]. The substrate molecular will break at these points, forming some precursor intermediates toward formation of NH_4^+ such as an amide [52]. In this work, cleavage of the corresponding C—N bonds leads to the formation of benzamidine (BZMD). Further attack of HO• could either oxidize BZMD to benzamide or form hydroxylated benzamidine (OH-BZMD). Note that two isomers of OH-BZMD were detected according to LC–MS analysis, which possibly resulted from *para-* and *ortho-*addition because of the electron donating effect of amidine moiety. *Para*-hydroxyl benzamidine has been known to absorb appreciably at 300 nm [53], which was confirmed in our HPLC–DAD chromatogram. It is also possible that OH-BZMD arose from the C—N bonds rupture of mono-hydroxylated PBSA. BZMD has been observed previously in PBSA photolysis as an important intermediate [14]. However, it was not detected in this work, probably due to a rapid transformation under HO• attack. During TiO_2 photocatalysis process,

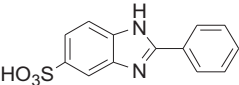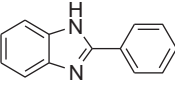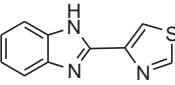benzamide could further transform to 4-hydroxyl benzamide and hydroquinone followed by ring opening [54].

(III) Pathway III is initiated by the detachment of sulfonic moiety in benzimidazole group, which consequently converts to sulfate. The detection of sulfate ions by ion chromatography (IC) verified the feasibility of such process. The de-sulfonic product 2-phenyl-1H-benzimidazole (PBI) further undergoes hydroxylation under the successive HO• attack. The hydroxylated PBI (OH-PBI) is supposed to generate 2-phenyl-4-carboxyl-5-aldehyde imidazole via benzene ring opening under further HO• attack. Similar benzene ring opening has been previously observed during photocatalytic degradation of thiabendazole, one kind of benzimidazole derivative fungicide which has similar structure with PBI [55]. Further oxidation of the aldehyde group generated 2-pheny-4,5-imidazoledicarboxylic acid, which subsequently lost one carboxyl group through photo-Kolbe mechanism to form two isomers of 2-pheny-imidazole carboxylic acid. It should be emphasized that some intermediate products (i.e., phenylimidazolecarboxylic derivatives and benzamide) were also observed by Zhang et al. in direct photolysis of PBSA [14], suggesting the similar degradation pathways are possibly involved in photolysis and photocatalysis.

3.6. Comparison to structurally related compounds

To obtain a further insight into the mechanism of photocatalysis, PBSA was compared to benzimidazole (BI), 2-phenyl-1H-benzimidazole (PBI) and 2-(4-thiazolyl)-1H-benzimidazole (thiabendazole) in photocatalytic degradation because these compounds have a benzimidazole ring in common. Table 3 compares the experimental results of photocatalytic degradation of these benzimidazole analogs under identical conditions. PBI has the same molecular structure as PBSA except that the latter has a sulfonic moiety linking to the benzimidazole ring. Due to the electron-withdraw effect, the lack of sulfonic moiety in PBI was expected to facilitate its photocatalytic degradation via HO• attack. However, no enhancement in photocatalytic degradation rate of PBI was observed in comparison to PBSA (Table 3), suggesting 5-sulfonic moiety in PBSA had negligible effect on the photocatalysis of PBI. Previous studies have demonstrated that the two compounds actually have very similar photophysical and photochemical properties [13]. This result was also supported by the fact that the possibility of HO• attacking on 2-phenyl group is much higher than benzyl group in PBSA as illustrated by FEDs calculation. PBI has also known to be a product of PBSA upon photolysis, however, it was not detected by LC-MS in this work. BI photocatalytically degraded at a rate constant approximately 1.6 times faster than PBSA and PBI (Table 3). This result was unexpected and interesting. Due to the 2-phenyl substitution in PBSA and PBI, and the electrophilic and nonselective nature of HO•, we postulated that the photocatalytic degradation of PBSA and PBI would have processed much more rapidly than BI because 2-phenyl provided additional sites for HO• attack. However, BI was found to be more susceptible to photocatalytic destruction. It is possible that 2-phenyl substitution enabled BI molecular being more resistant to photocatalytic degradation.

A noticeable peak corresponding to the photoproduct was found in the HPLC–DAD chromatogram of the irradiated PBI sample. Although further LC–MS analysis is necessary for the accurate identification of this photoproduct, its nearly identical UV–vis spectrum relative to the mother compound as well as the early retention time implied that this photoproduct was most likely to be the hydroxylated product. This result was consistent with the Pathway III proposed in Fig. 6. A similar peak was also observed in the case of BI. The evolution of the photoproducts of PBI and BI during photocatalysis process was also depicted in Fig. S5 (Supplementary Data).

Table 3
Photocatalytic degradation of PBSA and structurally related compounds.

Compounds	Molecular structure	Degradation rate constant (min^{-1})[a]	Linear correlation coefficient (R^2)
2-Phenylbenzimidazole-5-sulfonic acid (PBSA)		0.0381 ± 0.0026	0.999
Benzimidazole (BI)		0.0591 ± 0.0064	0.980
2-Phenyl-1H-benzimidazole (PBI)		0.0352 ± 0.0022	0.996–0.999
2-(4-thiazolyl)-1H-Benzimidazole (thiabendazole)[b]		NA[c]	NA

[a] Experimental conditions: Degussa P25 TiO_2 was used as photocatalyst; [substrate] = 45 μM; [TiO_2] = 1.0 g L^{-1}; pH = 7.0. Errors are 95% confidence intervals.
[b] Photocatalytic degradation pathways of thiabendazole was compared to PBSA according to Ref. [55].
[c] NA = not available. No kinetic data of thiabendazole photocatalysis was available in Ref. [55].

Note that the evolution profiles were only qualitative because there were no standards available of the photoproducts to ensure their quantitative analysis.

On the other hand, thiabendazole, a widely used fungicide, has a thiazole ring adjacent to benzimidazole ring instead of a phenyl ring in PBI. A previous study on identification of thiabendazole photo-transformation products on TiO_2 by Calza et al. showed that there are two different parallel pathways: (i) the hydroxylation of the molecular on the aromatic ring, a further oxidation leads to ring opening and to the formation of aldehydic and alcoholic structure; (ii) the cleavage of a C—C bond and the formation of benzimidazole [55]. It is apparent that Pathway I was identical to the Pathway III as we proposed in photocatalytic degradation of PBSA in this work (Fig. 6). However, the cleavage of the bond between benzimidazole and phenyl ring was not observed in the present study, which differed from thiabendazole in photocatalytic degradation. This finding can be explained by the strong π–π conjugation of benzimidazole and phenyl ring, resulting in the bond being stable. Similar result has been observed previously by a study on photolysis of various 2-substitued benzimidazoles [56]. It has been proposed that 2-phenyl group stabilizes the benzimidazole ring system to photolysis as does the 2-thiazolyl group; however, the latter suffers thiazole ring cleavage [56]. This finding also supported the above result that BI was substantially more susceptible to photocatalytic degradation compared to PBSA and PBI.

4. Conclusions

The aqueous photocatalytic degradation of sunscreen agent 2-phenylbenzimidazole-5-sulfonic acid (PBSA) has been studied in illuminated TiO_2 suspensions. TiO_2-induced photocatalysis resulted in a pronounced degradation of PBSA. Photocatalytic reactions followed pseudo-first-order kinetics. Radical scavenger experiments indicated that HO• was the predominant radical responsible for an appreciable degradation of PBSA. Second-order rate constant of PBSA-HO• reaction was determined to be 5.8×10^9 M^{-1} s^{-1} by competition kinetics method, suggesting HO•-mediated PBSA oxidation is near the diffusion-controlled limit. Organic intermediates were identified by LC–MS analysis, and the major photoproducts included hydroxylated products, imidazole ring cleavage compounds and phenylimidazolecarboxylic derivatives. Frontier electron densities (FEDs) calculation predicted that both the two benzenes in PBSA are likely to be attacked by HO•, resulting in the formation of mono-hydroxylation products. Four carboxylic acids, oxalic, malonic, acetic and maleic acids were detected during PBSA photocatalysis. Sulfonic moiety of PBSA was primarily released as a sulfate ion while nitrogen atoms were converted predominantly to ammonium and a less extent to nitrate. Approximately 80% TOC was removed after 720 min irradiation, implying mineralization can be expected to obtain after a very long irradiation time. A comparative study on photocatalytic degradation of PBSA and structurally related compounds revealed that the 5-sulfonic moiety had negligible effect on the photocatalysis while 2-phenyl substituent stabilized the benzimidazole ring system to photocatalytic degradation.

Although results from the present study suggest that TiO_2 photocatalysis is a promising treatment technology for sunscreen agent PBSA, a thorough evaluation of the toxicity of intermediates is essential in order to optimize photocatalytic treatment and evaluate the potential risks to the ecology system before the technology is applied for water purification.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2013.04.046.

References

[1] F.P. Gasparro, Environmental Health Perspectives 108 (2000) 71–78.
[2] T. Poiger, H.R. Buser, M.E. Balmer, P.A. Bergqvist, M.D. Müller, Chemosphere 55 (2004) 951–963.
[3] C. Plagellat, T. Kupper, R. Furrer, L.F. de Alencastro, D. Grandjean, J. Tarradellas, Chemosphere 62 (2006) 915–925.

[4] P. Gago-Ferrero, M. Silvia Díaz-Cruz, D. Barceló, Analytical Methods 5 (2013) 355–366.

[5] R.P. Schwarzenbach, B.I. Escher, K. Fenner, T.B. Hofstetter, C. Annette Johnson, U. von Gunten, B. Wehrli, Science 313 (2006) 1072–1077.

[6] M. Schlumpf, P. Schmid, S. Durrer, M. Conscience, K. Maerkel, M. Henseler, M. Gruetter, I. Herzog, S. Reolon, R. Ceccatelli, O. Faass, E. Stutz, H. Jarry, W. Wuttke, W. Lichtensteiger, Toxicology 205 (2004) 113–122.

[7] M. Silvia Díaz-Cruz, D. Barceló, Trends in Analytical Chemistry 28 (2009) 708–716.

[8] M. Silvia Díaz-Cruz, M. Llorca, D. Barceló, Trends in Analytical Chemistry 27 (2008) 873–887.

[9] C.G. Daughton, T.A. Ternes, Environmental Health Perspectives 107 (1999) 907–938.

[10] R. Rodil, J.B. Quintana, P. López-Mahía, S. Muniategui-Lorenzo, D. Prada-Rodríguez, Analytical Chemistry 80 (2008) 1307–1315.

[11] E. Gilbert, F. Pirot, V. Bertholle, L. Roussel, F. Falson, K. Padois, International Journal of Cosmetic Science (2013), http://dx.doi.org/10.1111/ics.12030.

[12] M. Krause, A. Klit, M. Blomberg Jensen, T. Søeborg, H. Frederiksen, M. Schlumpf, W. Lichtensteiger, N.E. Skakkebaek, K.T. Drzewiecki, International Journal of Andrology 35 (2012) 424–436.

[13] J. Johnson Inbaraj, P. Bilski, C.F. Chignell, Photochemistry and Photobiology 75 (2002) 107–116.

[14] S. Zhang, J. Chen, X. Qiao, L. Ge, X. Cai, G. Na, Environmental Science and Technology 44 (2010) 7484–7490.

[15] S. Zhang, J. Chen, Y. Wang, X. Wei, Environmental Chemistry Letters 10 (2012) 389–394.

[16] J.-M. Herrmann, Catalysis Today 53 (1999) 115–129.

[17] M. Nan Chong, B. Jin, C.W.K. Chow, C. Saint, Water Research 44 (2010) 2997–3027.

[18] Y. Chen, C. Hu, X. Hu, J. Qu, Environmental Science and Technology 43 (2009) 2760–2765.

[19] A.A. Khodja, B. Lavedrine, C. Richard, T. Sehili, International Journal of Photoenergy 4 (2002) 147–151.

[20] M.M. Haque, M. Muneer, D.W. Bahnemann, Environmental Science and Technology 40 (2006) 4765–4770.

[21] D.C. Hurum, A.G. Agrios, K.A. Gray, Journal of Physical Chemistry B 107 (2003) 4545–4549.

[22] J. Ryu, W. Choi, Environmental Science and Technology 42 (2008) 294–300.

[23] Y.F. Rao, W. Chu, Environmental Science and Technology 43 (2009) 6183–6189.

[24] J. Kim, C.W. Lee, W. Choi, Environmental Science and Technology 44 (2010) 6849–6854.

[25] H. Park, Y. Park, W. Kim, W. Choi, Journal of Photochemistry and Photobiology C: Photochemistry Review (2012), http://dx.doi.org/10.1016/j.jphotochemrev.2012.10.001.

[26] Y. Sun, J.J. Pignatello, Environmental Science and Technology 29 (1995) 2065–2072.

[27] Y. Chen, S. Yang, K. Wang, L. Lou, Journal of Photochemistry and Photobiology A: Chemistry 172 (2005) 47–54.

[28] S.T. Martin, A.T. Lee, M.R. Hoffmann, Environmental Science and Technology 29 (1995) 2567–2573.

[29] L. Yang, L.E. Yu, M.B. Ray, Environmental Science and Technology 43 (2009) 460–465.

[30] E. Hapeshi, A. Achilleos, M.I. Vasquez, C. Michael, N.P. Xekoukoulotakis, D. Mantzavinos, D. Kassinos, Water Research 44 (2010) 1737–1746.

[31] M. Sleiman, P. Conchon, C. Ferronato, J.-M. Chovelon, Applied Catalysis B: Environmental 71 (2007) 279–290.

[32] S. Ahmed, M.G. Rasul, R. Brown, M.A. Hashib, Journal of Environment Management 92 (2011) 311–330.

[33] B. Abramović, D. Šojić, V. Despotović, D. Vione, M. Pazzi, J. Csanádi, Applied Catalysis B: Environmental 105 (2011) 191–198.

[34] X. Lin, C. Ferronato, N. Deng, F. Wu, J.-M. Chovelon, Applied Catalysis B: Environmental 88 (2009) 32–41.

[35] L. Lagunas-Allué, M.-T. Martínez-Soria, J. Sanz-Asensio, A. Salvador, C. Ferronato, J.-M. Chovelon, Applied Catalysis B: Environmental 98 (2010) 122–131.

[36] J. Radjenović, C. Sirtori, M. Petrović, D. Barceló, S. Malato, Applied Catalysis B: Environmental 89 (2009) 255–264.

[37] C. Sirtori, A. Agüera, W. Gernjak, S. Malato, Water Research 44 (2010) 2735–2744.

[38] J.P. Huang, S.A. Mabury, Environmental Toxicology and Chemistry 19 (2000) 2181–2188.

[39] P.L. Brezonik, J. Fulkerson-Brekken, Environmental Science and Technology 32 (1998) 3004–3010.

[40] L. Hu, P.M. Flanders, P.L. Miller, T.J. Strathmann, Water Research 41 (2007) 2612–2626.

[41] N. Corin, P. Backlund, M. Kulovaara, Chemosphere 33 (1996) 245–255.

[42] K. Fukui, T. Yonezawa, H. Shingu, Journal of Chemical Physics 20 (1952) 722–725.

[43] K. Fukui, T. Yonezawa, T. Nagata, Journal of Chemical Physics 22 (1954) 1433–1442.

[44] Y. Ohko, K. Iuchi, C. Niwa, T. Tatsuma, T. Nakashima, T. Iguchi, Y. Kubota, A. Fujishima, Environmental Science and Technology 36 (2002) 4175–4181.

[45] P. Calza, C. Medana, C. Baiocchi, E. Pelizzetti, Journal of Photochemistry and Photobiology A 189 (2007) 380–386.

[46] H. Yang, G. Li, T. An, Y. Gao, J. Fu, Catalysis Today 153 (2010) 200–207.

[47] E. Szabó-Bárdos, O. Markovics, O. Horváth, N. Töró, G. Kiss, Water Research 45 (2011) 1617–1628.

[48] M. Sleiman, D. Vildozo, C. Ferronato, J.-M. Chovelon, Applied Catalysis B: Environmental 77 (2007) 1–11.

[49] L. Lagunas-Allué, M.-T. Martínez-Soria, J. Sanz-Asensio, A. Salvador, C. Ferronato, J.-M. Chovelon, Applied Catalysis B: Environmental 115–116 (2012) 285–293.

[50] F. Méndez-Arriaga, S. Esplugas, J. Giménez, Water Research 42 (2008) 585–594.

[51] H. Hidaka, E. García-López, L. Palmisano, N. Serpone, Applied Catalysis B: Environmental 78 (2008) 139–150.

[52] E. Pelizzetti, P. Calza, G. Mariella, V. Maurino, C. Minero, H. Hidaka, Chemical Communications 13 (2004) 1504–1505.

[53] E. Rogana, D.L. Nelson, M. Mares-Guia, Journal of the American Chemical Society 97 (1975) 6844–6848.

[54] A. Piscopo, D. Robert, J.V. Weber, Journal of Photochemistry and Photobiology A: Chemistry 139 (2001) 253–256.

[55] P. Calza, S. Baudino, R. Aigotti, C. Baiocchi, E. Pelizzetti, Journal of Chromatography A 984 (2003) 59–66.

[56] G. Crank, A. Mursyidi, Australian Journal of Chemistry 35 (1982) 775–784.